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Flow-drift and selected ion flow tube techniques have been coupled with laser-induced fluorescence detection to explore the chemistry and dynamics of gas phase ion-molecule interactions. The charge transfer and atom abstraction rates of vibrationally excited ions have been studied, as well as the competition between deactivation and reaction. The reactions and energy transfer of the vibrationally excited molecular nitrogen cation with the rare gases and several diatomic molecules were explored in detail, and dramatic effects of vibrational enhancement were observed. The mobilities of atmospheric cluster ions were measured using the selected ion flow tube technique. Detailed systematizations of the results were made for both nonpolar and highly polar collision partners. Velocity-resolved measurements were made using a single frequency dye laser. It was determined that the rotational alignment resulting from the collisions of the nitrogen molecular cation, in its ground vibrational state, with helium at elevated kinetic energies is a dramatic function of the velocity subgroup probed.

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Table of Contents

Final Technical Report
"State Resolved Dynamics of Ion-Molecule Processes"
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(Grant Period: 1 November 1994 - 31 October 1997)
Stephen R. Leone and Veronica M. Bierbaum - Principal Investigators

Summary of Results

Ion chemistry plays a crucial role in the earth's atmosphere, the interstellar medium, lasers, etching processes and a variety of important analytical techniques. Moreover, studies of ion-neutral reactions advance our understanding of solution chemistry and aid in the evaluation and development of theory. With AFOSR support, we have developed many powerful and productive approaches to obtaining detailed information on ion-neutral processes. In the past three years, several innovative studies have been performed. A selected ion flow tube apparatus was used to study charge transfer and atom abstraction rates as well as the competition between deactivation and reaction of vibrationally excited ions. The reactions and energy transfer of vibrationally excited $N_2^+(v=0-4)$ with the rare gases and several diatomic molecules were studied in detail, exhibiting several dramatic effects of vibrational enhancement. The mobilities of several atmospheric cluster ions have been measured using the selected ion flow tube. Detailed systematizations of the results were made for both nonpolar and highly polar collision partners. Velocity-resolved measurements were made using a single frequency dye laser and it was determined that the rotational alignment resulting from the collisions of $N_2^+(v=0)$ with He at elevated kinetic energies is a dramatic function of the velocity subgroup probed. In this Final Technical Report, we enumerate the highlights of the last three-years' effort.

A. Vibrationally State Resolved Reactions

Our studies over the past several years have demonstrated that exoergic ion-molecule reactions can generate product ions with extensive vibrational excitation. These ions may exhibit enhanced reactivity, new reaction pathways or different product distributions and thus may have a dramatic impact on many chemical systems, including the chemistry of the earth's atmosphere. However, relatively little is known about the deactivation and reaction of vibrationally excited ions. Laboratory studies have been hampered by many problems; in particular, these ions are efficiently relaxed by their parent neutrals so that maintaining high concentrations is problematic. To overcome these difficulties, we have constructed a major new apparatus,[1] a selected ion flow tube instrument (SIFT) coupled with laser-induced fluorescence detection (LIF). Ions are generated in an electron-impact source, mass-selected and separated from neutral precursors, and injected into a flow tube where their vibrational distribution and reactivity at thermal energy are characterized by laser-induced fluorescence. Using this powerful new instrument, we have explored the deactivation and reactivity of $N_2^+(v)$ with a variety of species including He, Ne, Ar, Kr, Xe, N_2, O_2, H_2, CO, NO, and HCl. These studies are especially important and relevant to AFOSR interests since N_2^+ plays a central role in the ion chemistry of the earth's atmosphere.

1. Reactions of $^{14}N_2^+(v=1,2)$ and $^{15}N_2^+(v=0,1,2)$ with $^{14}N_2$

An especially intriguing question in the study of vibrationally excited ions involves the competition between charge transfer and vibrational energy transfer in symmetric systems such as $N_2^+(v) + N_2$. The new SIFT instrumentation makes these experiments feasible by the generation and mass-selection of isotopically labeled $^{15}N_2^+(v)$. We have found that the rate constant for $^{15}N_2^+(v=0) + ^{14}N_2$ is one-half of the Langevin collision rate, suggesting that the reaction proceeds via an N_4^+ energized adduct in which charge is shared on a time scale shorter than the adduct lifetime.[2] The removal rates of $^{14}N_2^+(v=1$ and $2)$ by reaction with $^{14}N_2$ are also one-half of the collision values; thus product channels that remove vibrational energy from the ion upon dissociation of the adduct account for 50% of the collision probability. The removal rates of $^{15}N_2^+(v=1$ and $2)$ with $^{14}N_2$ are about 25% faster than those for $^{14}N_2^+(v=1$ and $2)$; this is attributed to the previously undetected channel in which both charge and vibrational energy are transferred between the collision partners.[2]

2. Reactions of $N_2^+(v)$ with Ar and O_2

The charge transfer reaction of $N_2^+(v=0)$ with Ar is slow, whereas the corresponding reactions of $N_2^+(v=1, 2, 3,$ and $4)$ are rapid (~0.5 Langevin rate) and show little dependence on vibrational level. The dramatic rate enhancement is due exclusively to an increase in the charge transfer channel. The rate constants are quantitatively described by a simple model based on energy resonance and a set of modified Franck-Condon factors, which take into account the change in vibrational wave functions of N_2^+ and N_2 at short $(N_2-Ar)^+$ distances.[3] The total rate constant for $N_2^+(v=1,2) + O_2$ increases by factors of 2.6 and 3.3, respectively, relative to the charge transfer reaction of $N_2^+(v=0)$.[4] In contrast to the $N_2^+(v) + Ar$ reaction, this enhancement is largely due to the occurrence of vibrational deactivation, which is found to be slightly faster for $v=2$ than for $v=1$.

3. Reaction of $N_2^+(v)$ with H_2

The hydrogen atom transfer reaction between $N_2^+(v)$ and H_2 to form N_2H^+ and H has been studied as a function of the initial vibrational excitation of the N_2^+ molecular ion.[5] The rate constant is approximately the same for $v=0, 1, 2,$ and 3 and is slightly smaller for $v=4$. The absolute values exceed the Langevin rate, in good agreement with previous studies. The observations are consistent with a mechanism in which charge transfer at large intermolecular distances precedes the formation of N_2H^+. Vibrational deactivation does not occur on the short time scale of these reactive processes.

4. Reaction of $N_2^+(v=0-4)$ with Kr

We have observed a dramatic vibrational enhancement in the charge transfer rate constant for $N_2^+(v) + Kr$, as shown in Fig. 1.[6] Charge transfer for $v=0$ is extremely slow in spite of the large exothermicity, yet the reaction is enhanced when the apparent energy mismatch is greater for the vibrationally excited reactant. A simple model is proposed to explain the experimental results at thermal energies. The model assumes that only the most energy-resonant exothermic transitions, $N_2^+(v) + Kr \rightarrow N_2(v+3) + Kr^+(^2P_{1/2})$, occur within the duration of the ion-molecule collision complex and that the charge transfer takes place with probabilities governed by the corresponding Franck-Condon factors. However, the Franck-Condon factors are modified by a small displacement (0.002 nm) to account for the changes in vibrational wave functions of N_2^+ and N_2 during a close approach of the $(N_2-Kr)^+$ pair, giving an excellent description of the experimental results.
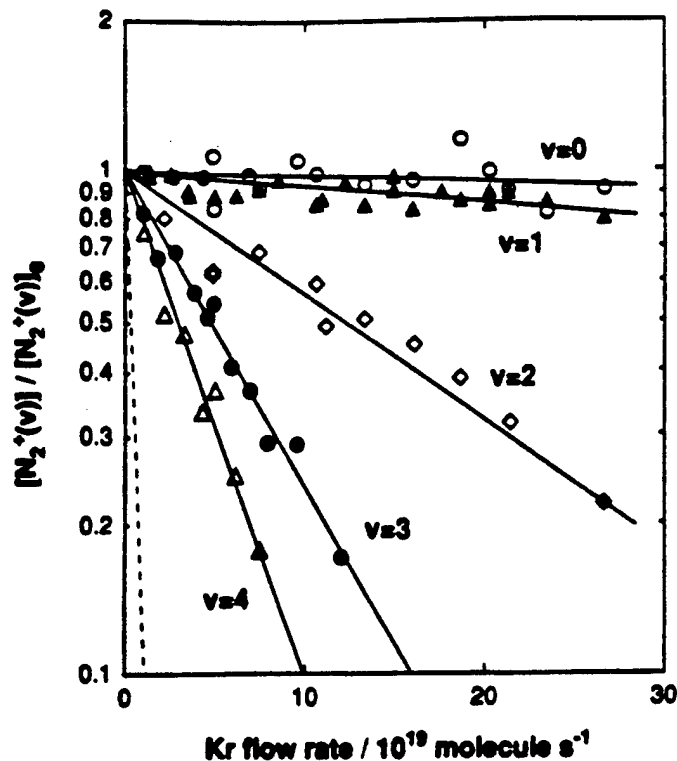
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Figure 1. LIF kinetics plots for $N_2^+(v=0-4)$ with Kr. The broken line represents the decay at the Langevin collision rate (8.1×10^{-10} cm³ molecule⁻¹ s⁻¹).

5. Vibrational Relaxation of $N_2^+(v)$ with He, Ne, Ar, Kr, and Xe

We have combined the SIFT-LIF technique with conventional mass spectrometry to measure accurately the extremely small rate constants for vibrational relaxation of $N_2^+(v)$ with He, Ne, Ar, Kr, and Xe.[7] Our results, summarized in Table 1, provide the first measurement for relaxation by Ar, and provide substantial refinements[8-11] in the rate constants for relaxation by He, Ne, Kr, and Xe. The small deactivation probabilities, ranging from 1.7×10^{-6} for He to 1.6×10^{-4} for Xe, are discussed in terms of two types of relaxation mechanisms. The correlation between the rare gas polarizability and the relaxation rate constant strongly suggests the importance of attractive forces in the vibrational relaxation. A direct impulsive mechanism may be operative for the vibrational relaxation of $N_2^+(v)$ with He.

6

Table 1. Rate Constants for $N_2^+(v)$ Vibrational Relaxation with Rare Gases[a]

	He	Ne	Ar	Kr	Xe
This work[b] (SIFT–LIF)	$9.8(\pm0.7) \times 10^{-16}$	$3.6(\pm0.5) \times 10^{-14}$	$<1.2 \times 10^{-11}$	$<2 \times 10^{-12}$	$1.6(\pm0.2) \times 10^{-13}$
Previous (SIFT/SIFDT)	$5(^{+4}_{-2}) \times 10^{-15}$ [c]	4.5×10^{-12} [d]	–	$5(^{+5}_{-2.5}) \times 10^{-12}$ [e]	–
Previous (TICR)[f]	$2.2(\pm3) \times 10^{-12}$	$5.5(\pm5) \times 10^{-12}$	–	$1.10(\pm0.85) \times 10^{-11}$	$1.45(\pm0.7) \times 10^{-1}$

a. k_q in units of cm^3 molecule^{-1} s^{-1}.
b. Errors reported represent one standard deviation in fitting the data.
c. Ref. 8, error bar estimated from the scatter in the data of Fig. 5 in Ref. 8.
d. Ref. 9, error bar specified as ±30%.
e. Drift tube data at $E_{cm} = 0.05$ eV (Ref. 10).
f. Tandem ion cyclotron resonance (Ref. 11).

6. Reaction of $N_2^+(v=0\text{-}3)$ with HCl

The rate constant and product branching ratio for the reaction $N_2^+(v=0\text{-}3)$ + HCl show little or no dependence on vibrational excitation.[12] In addition, vibrational deactivation of the N_2^+ molecular ion is not significant, representing at most 20% of the total removal rate. The results are understood by a model in which an ion-molecule complex is formed at the collision rate, and there is only weak coupling of the vibrational excitation into the collision complex bond.

7. Reaction of $N_2^+(v)$ with CO and NO

The charge transfer and vibrational relaxation reactions of $N_2^+(v=0, 1,$ and $2)$ with CO and NO have been studied.[13] For $N_2^+(v)$ reactions with CO it is found that $N_2^+(v>0)$ ions are removed with rate constants ~2.4 times faster than that for $N_2^+(v=0)$ removal.. The measurements indicate that the increased reactivity of $N_2^+(v>0)$ is accounted for by both enhanced charge transfer and vibrational relaxation. In collisions with NO, $N_2^+(v>0)$ ions are removed with rate constants ~1.7 times the observed rate constant for $N_2^+(v=0)$ removal. Only a minor increase in the charge transfer cross section is inferred for ion vibrational excitation. Rather, most of the additional rate of removal of $N_2^+(v>0)$ arises from vibrational relaxation. The efficient vibrational relaxation in this system is explained by the long lifetime of the energized adduct.

B. Mobilities of Cluster Ions

Cluster ions play an important role in the ion chemistry of the earth's atmosphere. For example, clusters with NO^+, H_3O^+ and NH_4^+ as core ions, and with H_2O, NH_3 or CH_3CN as solvating ligands, among many others, have been detected in the earth's troposphere, stratosphere

and ionosphere. Although the association and dissociation processes forming these ions are in general well-understood, the mobilities of these cluster ions remain largely uncharacterized. These values are essential, not only in modeling atmospheric phenomena, but also in providing direct information about the ion-buffer gas interaction potential.

Our selected ion flow tube apparatus has been modified to include a well-defined flow drift region and instrumentation for ion modulation and data acquisition. Core ions are generated in an ion source, mass-selected and injected into the flow tube where they associate with added solvent molecules before entering the drift region. Two drift rings, at known separation, are simultaneously pulsed; the resulting ion depletions are detected with a quadrupole mass filter in a time-resolved manner, as a function of E/N. We have completed studies of the mobilities of two important families of atmospheric cluster ions, $NO^+(CH_3CN)_n$ and $NH_4^+(NH_3)_n$ (n=0-3), and of several prototypical aromatic species.

1. Mobilities of $NO^+(CH_3CN)_n$ Cluster Ions

The mobilities of $NO^+(CH_3CN)_n$ cluster ions (n=0-3) drifting in helium and in mixtures of helium and acetonitrile (CH_3CN) have been measured in the SIFT-drift instrument.[14] The mobilities in helium decrease with cluster size, as shown in Table 2, and depend only weakly on the characteristic parameter E/N. The size dependence is explained in terms of the geometric cross sections of the different cluster ions. The rate constants for the various cluster formation and dissociation reactions have also been determined in order to rule out the possibility that reactions occurring in the drift region influence the measurements in the mixtures. In addition, several experiments were carried out in a flowing afterglow source-SIFT-drift instrument (FA-SIFDT), in which mass-selected cluster ions can be injected for study in pure helium. These measurements provided a consistent set of results.

Since high pressures of acetonitrile are required to form $NO^+(CH_3CN)_2$ and $NO^+(CH_3CN)_3$, the mobilities of these ions are found to be dependent on the acetonitrile concentration, as a result of anomalously small mobilities of these ions in acetonitrile. These mobilities are deduced using Blanc's law and are summarized in Table 2. These values are at least an order of magnitude smaller than any previously reported ion mobility, which can be partly explained by the large ion-permanent dipole interaction between the cluster ions and acetonitrile. The remaining discrepancies may be the result of momentum transfer outside the capture cross section, dipole-dipole interactions, ligand exchange, the formation of long-lived collision complexes or the transfer of kinetic energy into internal energy of the cluster ion and acetonitrile molecule.

8

Table 2. **Reduced zero-field mobilities (cm^2 V^{-1} s^{-1}) of NO$^+$(CH$_3$CN)$_n$ in collision gas M at 300K**

M	n=0	n=1	n=2	n=3
He	22.4 ± 0.5	12.3 ± 0.3	8.2 ± 0.2	7.5 ± 0.5
CH$_3$CN			0.041 ± 0.004	0.044 ± 0.004

2. Mobilities of NH$_4^+$(NH$_3$)$_n$ Cluster Ions

Ammonia and its cluster ions have been detected in the earth's troposphere, the lowest 10-15 km of the earth's atmosphere. We have studied the formation and dissociation kinetics of the NH$_4^+$(NH$_3$)$_n$ cluster ions and demonstrated that these reactions do not affect the mobility measurements. Experiments were carried out using both SIFDT and FA-SIFDT instrumentation, and the results are in good agreement. Although the dipole moment of NH$_3$ (1.471 D) is smaller than that of CH$_3$CN (3.924 D), the mobility values of the cluster ions were found to depend on ammonia concentration. Therefore, zero field mobilities both in helium and in ammonia were determined and are summarized in Table 3.[15]

Table 3. **Reduced zero-field mobilities (cm^2 V^{-1} s^{-1}) of NH$_4^+$(NH$_3$)$_n$ in collision gas M at 300K**

M	n=0	n=1	n=2	n=3
He	22.1 ± 0.4	16.6 ± 0.4	12.2 ± 0.4	12.1 ± 0.4
NH$_3$	0.94 ± 0.35	0.83 ± 0.22	0.50 ± 0.27	0.25 ± 0.20

3. Mobilities of Aromatic Ions

We have determined the mobilities of several prototypical aromatic ions drifting in helium, including C$_6$H$_5^+$ [11.7 ± 0.4 cm^2 V^{-1} s^{-1}], C$_6$H$_6^+$ [11.8 ± 0.3 cm^2 V^{-1} s^{-1}], C$_6$H$_7^+$ [11.6 ± 0.4 cm^2 V^{-1} s^{-1}], C$_{12}$H$_{12}^+$ [7.6 ± 0.3 cm^2 V^{-1} s^{-1}] C$_{12}$H$_{11}^+$ [7.8 ± 0.3 cm^2 V^{-1} s^{-1}], naphthalene cation (C$_{10}$H$_8^+$) [8.8 ± 0.3 cm^2 V^{-1} s^{-1}], and biphenyl (C$_{12}$H$_{10}^+$) [7.6 ± 0.3 cm^2 V^{-1} s^{-1}].[16] These results demonstrate that the compact rigid structure of the naphthalene cation is readily distinguished from the more bulky, less rigid structures of the biphenyl cation and of the benzene dimer cation. In

addition, calculated mobilities suggest that, for the benzene dimer cation, the sandwich structure is slightly favored over the axial T-type structure.

4. Mobilities of Ions in Helium - the Hard Sphere Collision Model

Angle-averaged hard sphere collision cross sections have been calculated from the geometric structures of the cluster ions described above as well as for the $H_3O^+(H_2O)_n$ system. These values have been used to compute the zero-field mobilities of the cluster ions in helium. As shown in Fig. 2,[17] the predicted mobilities, indicated by the solid curve, are in good agreement with the experimentally measured values. Ion-induced dipole interactions, indicated by the dashed line, are important only for the smallest ions drifting in helium.
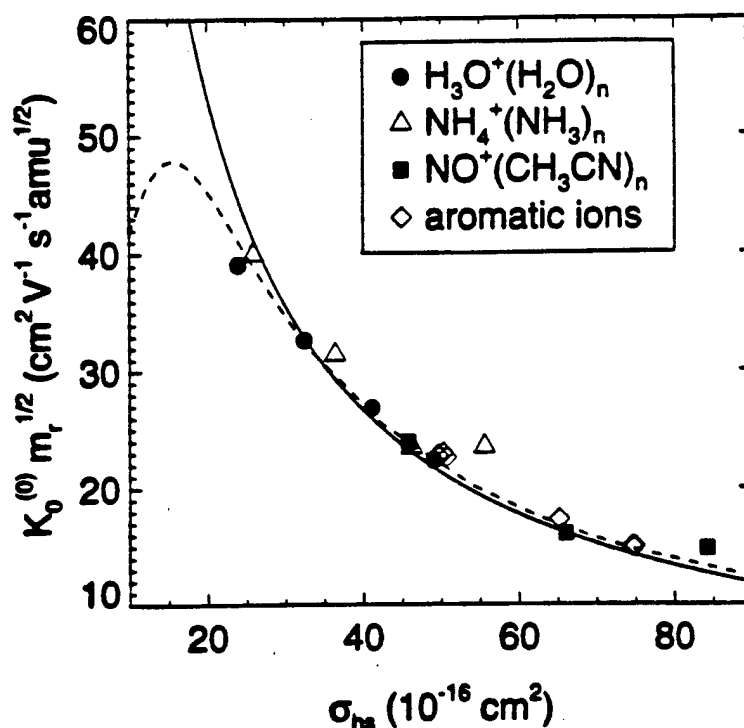

Figure 2. Cluster ion mobilities in He at 300 K vs. the angle-averaged hard-sphere cross section of the ions. The solid curve represents the hard-sphere collision model; the dashed curve includes ion-induced dipole attraction.

5. Mobilities of Ions in Polar Gases

The mobility of ions drifting in polar gases is an intriguing but relatively unexplored area; our SIFDT experiments have provided important new results and understanding. We have recently

extended a number of theoretical models which describe capture in ion polar-molecule collisions to the calculation of ion mobilities.[18] The model specifically addresses the ion-dipole (μ) interaction, which makes a large contribution, as well as the ion-polarizability (α) interaction. Figure 3 demonstrates that reasonable agreement is obtained between these calculated mobilities and the available experimental data. Remaining discrepancies may be due to the failure of the capture cross section to describe the momentum-transfer cross section, dipole-dipole interactions, ligand-exchange reactions, inelastic collisions and the validity of Blanc's law.
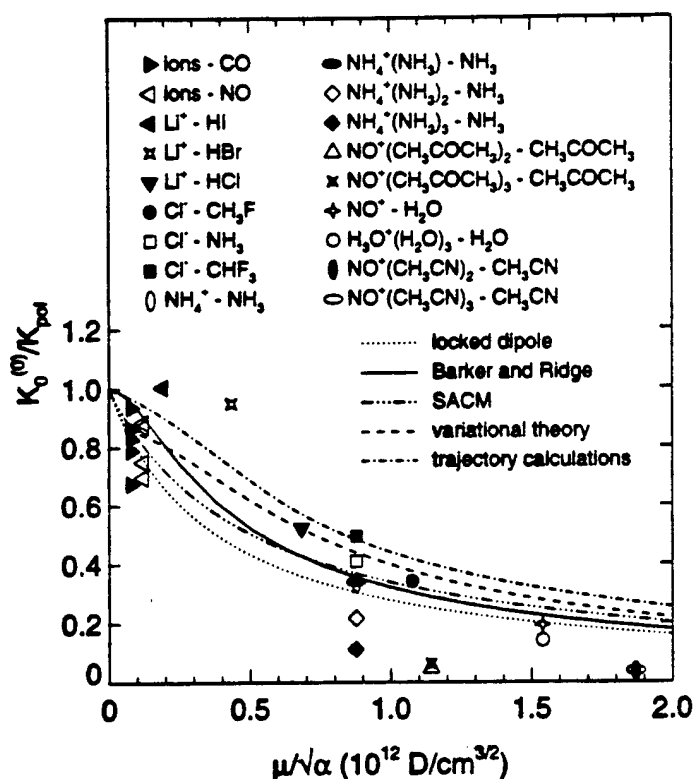
Figure 3. The ratio between the measured and calculated zero-field mobilities $K_0^{(0)}$ and the polarization limit K_{pol} as a function of the parameter $\mu/\sqrt{\alpha}$ at 300 K.

C. Laser Doppler Probing of Ion Alignment and Mobility

There is increased interest in the role of internal states and molecular anisotropies on the dynamics of both ion and neutral[19-22] transport properties, neither of which are readily predicted by

simple theory. Tunable, single frequency lasers have been used to measure Doppler velocity profiles of ions in plasma environments[23-25] and are extended here to measure molecular alignments and velocity profiles in a drift tube. Our group has performed a number of unique experiments using a single frequency tunable cw laser to characterize the microscopic basis of the velocity distributions, including the mean of the distribution or mobility, the width or temperatures parallel and perpendicular to the drift direction, the skewness, and correlations between the parallel and perpendicular motions.[26-30]

Figure 4 shows the Doppler line profiles for the $N_2^+(v=0)$, $R_1(15)$ line in He at several field strengths, E/N of 0, 8, and 16 Td.[31] From the mean values of these Doppler data, after correction for the underlying hyperfine structure, the ion mobility as a function of field strength is obtained. Contrary to earlier preliminary results on CO^+ in He,[32] the results of the mobility for N_2^+ measured by the laser Doppler shift technique and those reported earlier by the arrival time method described above are in good agreement. The better agreement is attributed to the substantially improved signal-to-noise ratio in the N_2^+ experiments. The results also provide a measure of the line broadening, or second central moment of the velocity distribution, which reflects the temperatures of the ions parallel and perpendicular to the drift field. For N_2^+ in He, the parallel temperature is considerably higher than the perpendicular temperature (e.g., 554 K vs. 432 K at 16 Td), also in contrast to the results for CO^+ in He,[29] where the parallel and perpendicular temperatures appeared similar, albeit the CO^+ results were obtained on different rotational states.
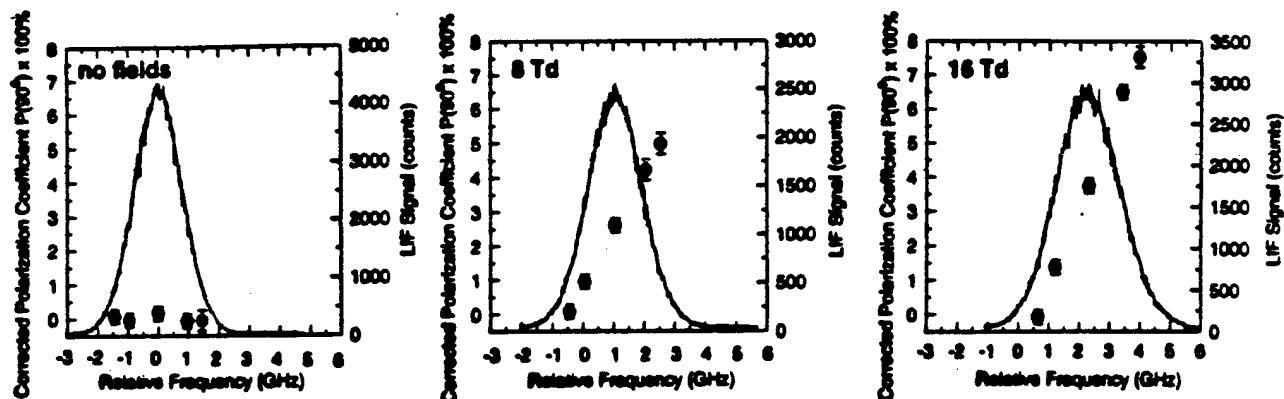

Fig. 4 Doppler profiles of $N_2^+(v=0)$ $R_1(N''=15)$ at three field strengths showing the raw polarizations of the alignment.

In addition, there is a clear indication that the N_2^+ velocity distribution has a skewness or nonzero third central moment, which is the first time that a skewness has been observed for a molecular ion. All results agree with physical interpretations and elucidate a number of new principles for molecular ion transport.

A very early study in our laboratory using a pulsed laser to study N_2^+ drifted in He demonstrated that molecular ions can exhibit significant rotational alignment caused by collisions in the drift tube.[32] The ions were found to rotate with their plane of rotation preferentially aligned in the direction of the field. Both an anisotropy in the potential of interaction and in the velocity distribution are necessary to produce the rotational alignment. Supersonic expansions of gases also provide a strong velocity gradient that can align neutral molecules.[19-22,33-40]

Calculations on the alignment of N_2^+ in He were performed by Follmeg, Rosmus, and Werner[41,42] using the steady-state formalism developed by Meyer and Leone[43] and the tensor cross sections calculated by Follmeg *et al.* for elastic and inelastic alignment-dependent scattering. Provocatively, the calculations predicted a significantly smaller alignment for N_2^+ in He than observed. At the time of those calculations, it was necessary to estimate the velocity distribution, and it was also shown that the theoretical results are very sensitive to the velocity distribution used. The theory suggests that the resulting magnitude and direction of alignment (i.e., preferred plane of rotation) can depend on whether the attractive or repulsive parts of the interaction potential are sampled at different velocities.

Using the cw laser rather than the pulsed laser, an improvement in signal-to-noise of more than a factor of 100 over the pulsed experiments has been realized. We have now been able to probe the velocity dependent alignment as a function of velocity subgroup and found that the results are highly dependent on the velocity.

Figure 4 also shows the polarizations, or alignment, of the N_2^+ ions as they are drifted in He as a function of Doppler velocity.[31] Polarization measurements are taken with the linearly polarized laser and a polarization filter that is used to detect the fluorescence polarized at two angles, parallel and perpendicular to the field. The figure shows the raw observed polarizations, in which the laser is propagated parallel to the field in the horizontal direction, the laser polarization is vertical, and fluorescence is detected in the vertical direction with the polarization analyzer either parallel or perpendicular to the field. The figure clearly shows a dramatic dependence of the observed alignment on the velocity subgroup probed.

The observed polarization indicates that the plane of rotation of the N_2^+ molecule is

preferentially aligned parallel to the direction of the electric field. The raw polarizations are converted into quadrupole alignment moments $A_0^{(2)}$ after correction for depolarizing effects of the electron and nuclear spin. A maximum value of $A_0^{(2)} = -0.150$ is obtained, which is a substantial alignment. The results suggest that a hard ellipsoid picture may in fact be a reasonable model for this system. Since the well depth of the N_2^+---He attractive interaction potential is only about 15 meV, and this is less than the mean collision energy at room temperature [$(3/2)kT = 40$ meV], we believe that sampling of the repulsive part of the potential predominates at the higher collision energies in the drift field. This is in agreement with the fact that there is little or no mobility maximum observed for N_2^+ in He.[44] However, two underlying effects are occurring. One is the sampling of differing regions of the attractive or repulsive parts of the potential when the collision energy is changed, and the other is the change in the magnitude of the anisotropy of the velocity distribution itself with drift field. The more directional the velocity distribution, the greater the alignment can be. The increasing anisotropy of the velocity distribution is the most likely explanation for the results shown in Fig. 4, which is consistent with the weakly attractive N_2^+---He interaction. All collisions sample the repulsive part of the potential, but the higher the value of the velocity component selected in the direction parallel to the field, the greater is the overall anisotropy of the velocity distribution, since the random velocity components transverse to the field are essentially constant.

In addition, an analytical solution to the optical Bloch equations has been obtained to study the alignment detection using saturated coherent laser pulses.[45] It is shown for molecular species that significant alignment can be introduced by the saturating light field. Depending on the detuning from resonance and degree of saturation, this alignment can even switch directions. These results are important since many experimental groups use intense pulsed laser fields to probe alignment.

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